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(54) Hair Care Preparations

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HAIR CARE PREPARATIONS

This invention relates to hair-treatment preparations containing zwitterionic polymers.

After washing, dyeing, or permanent waving, hair often shows unsatisfactory wet and dry combability, in addition to which the curl retention capacity of dry hair is inadequate. To remedy this drawback, either appropriate components have to be added to the hair treatment preparations, or the hair has to be subsequently subjected to a separate treatment with these substances which, for this purpose, are normally formulated as a rinse.

10 Polymeric compounds are frequently used as active substances of the type in question to improve the properties of hair.

5 Although cationic polymers, such as for example the cellulose derivatives known from US Patents 3,816,616 and 3,472,840, are capable of distinctly improving wet combability, they effect only unsatisfactory hair-setting and style-holding effects.

10 The use of zwitterionic polymers containing anionic groups, mostly carboxyl groups, and quaternary ammonium groups in the molecule in hair-treatment preparations is also known. For example, DE-OS 21 50 557 describes the use of polymers of zwitterionic monomers in hair-setting preparations. The use of copolymers of dimethylaminoethyl methacrylate, acrylic acid and methyl methacrylate in hair-setting lotions and shampoos is also known from DE-OS 28 17 369.

15 These known zwitterionic polymers in hair-treatment and hair-setting preparations have the disadvantage, particularly in formulations with anionic surfactants, that their hair-conditioning and hair-setting properties are gradually lost in the event of prolonged storage. Accordingly, it was proposed in DE-OS 37 08 451 to use zwitterionic polymers consisting of 30 to 70% monomers containing quaternary ammonium groups, 10 to 30% monomeric olefinically unsaturated carboxylic acids, 10 to 30% monomeric olefinically unsaturated carboxylic acid esters and 0 to 40% monomers containing tertiary amino groups. These polymers are highly compatible with anionic and cationic surfactants and have good hair-conditioning and style-holding properties.

20 Although, therefore, suitable polymers are available for obtaining the desired effects on the hair, these polymers are made up of at least 3 or 4 monomers. Accordingly, there is still a need for polymers which, for comparable properties, are less complex in structure, i.e. can be synthesized from a smaller number of different monomers.

25 It has now surprisingly been found that certain zwitterionic polymers of monomers containing quaternary ammonium groups and monomeric carboxylic acids have wet-comba-

5 bility-improving, hair-conditioning and style-holding properties which, hitherto, have only been achieved with polymers of a larger number of different monomers. In addition, it is possible with these polymers to formulate hair-treatment preparations based on anionic and/or amphoteric surfactants which, on the basis of their effect on the wet combability of hair, correspond in their performance level to known cationic rinses.

10 Accordingly, the present invention relates to water-based hair-treatment preparations containing zwitterionic polymers, characterized in that the zwitterionic polymers are essentially made up of

15 A) monomers containing quaternary ammonium groups corresponding to general formula (I)

$$R^1-CH=CR^2-CO-Z-(C_nH_{2n})-N^{(+)R^3R^4R^5} A^{(-)} \quad (I)$$

in which R^1 and R^2 independently of one another represent hydrogen or a methyl group and R^3 , R^4 and R^5 independently of one another represent C_{1-4} alkyl groups, Z is an NH group or an oxygen atom, n is an integer of 2 to 5 and $A^{(-)}$ is the anion of an organic or inorganic acid

and

20 B) monomeric carboxylic acids corresponding to general formula (II)

$$R^6-CH=CR^7-COOH \quad (II)$$

in which R^6 and R^7 independently of one another are hydrogen or methyl groups.

25 Suitable starting monomers are, for example, dimethylaminoethyl acrylamide, dimethylaminoethyl methacrylamide, dimethylaminopropyl acrylamide, dimethylaminopropyl methacrylamide, and diethylaminoethyl acrylamide in cases where Z is an NH group or dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate, and diethylaminoethyl acrylate in cases where Z is an oxygen atom.

30 The monomers mentioned are prepared by known methods of the type described, for example, in US Patent 3,878,247, DE-PS 28 19 735, DE-PS 28 36 520, DE-PS 34 02 599 or CH-

PS 464 891.

The monomers containing a tertiary amino group are then quaternized in known manner, methyl chloride, dimethyl sulfate or diethyl sulfate being particularly suitable alkylating reagents. The quaternization reaction may take place in aqueous solution or in a solvent. Suitable processes are described, for example, in DE-OS 33 30 326, DE-OS 25 37 378, or DE-OS 32 44 274.

It is of advantage to use monomers corresponding to formula (I) which are derivatives of acrylamide or methacrylamide. Other preferred monomers are those which contain halide, methoxysulfate, or ethoxysulfate ions as counterions. Monomers of formula (I), in which R^3 , R^4 and R^5 are methyl groups, are also preferred.

Acrylamidopropyl trimethyl ammonium chloride is a particularly preferred monomer of formula (I).

Suitable monomeric carboxylic acids corresponding to formula (II) are acrylic acid, methacrylic acid, crotonic acid and 2-methyl crotonic acid. Acrylic acid or methacrylic acid are preferred, acrylic acid being particularly preferred.

The zwitterionic polymers according to the invention are prepared from monomers corresponding to formulae (I) and (II) by polymerization processes known *per se*. The polymerization may be carried out either in aqueous solution or in aqueous/alcoholic solution. The alcohols used are C_{1-4} alcohols, preferably isopropanol, which simultaneously act as polymerization regulators. However, other components may be added to the monomer solution as regulators, including for example formic acid or mercaptans, such as thioethanol and thioglycolic acid. The polymerization is initiated by radical-forming compounds. Redox systems and/or thermally decomposing radical formers of the azo compound type, such as for example azoisobutyronitrile, azo-bis-(cyanopentanoic acid) or azo-bis-(amidinopropane)-dihydrochloride, may be used for this purpose. Suitable redox systems are, for example, combinations of hydrogen

peroxide, potassium or ammonium peroxodisulfate and tertiary butyl hydroperoxide with sodium sulfite, sodium dithionite or hydroxylamine hydrochloride as reducing component.

5 The polymerization may be carried out isothermally or under adiabatic conditions, the reaction temperature being variable over the range from 20 to 200 ° C, depending on the concentrations used, through the heat of polymerization released. The reaction may have to be carried out under 10 the excess pressure spontaneously established. The reaction temperature is preferably in the range from 20 to 100 ° C.

15 The pH value during the copolymerization may vary over a wide range. Polymerization is advantageously carried out at low pH values, although it may also be carried out at pH values above the neutral point. On completion of polymerization, the reaction mixture is adjusted to a pH value of 5 to 10 and preferably 6 to 8 with an aqueous base, for example sodium hydroxide, potassium hydroxide or ammonia. 20 Further particulars of the polymerization process can be found in the Examples.

25 Polymers in which the monomers of formula (I) were present in an excess over the monomers of formula (II) have proved to be particularly effective. In a preferred embodiment of the invention, therefore, the polymers used consist of monomers corresponding to formula (I) and monomers corresponding to formula (II) in a molar ratio of 60:40 to 95:5 and, more particularly, 75:25 to 95:5.

30 The zwitterionic polymers mentioned are preferably present in the preparations according to the invention in quantities of 0.1 to 10% by weight, based on the preparation as a whole. The polymers are very effective in improving wet combability, even in low concentrations. By contrast, their hair-conditioning and hair-setting effects 35 in most cases are only observed with concentrations above about 1 % by weight. Accordingly, it is particularly preferred to use the polymers in quantities of about 1 to 5%

by weight.

5 The zwitterionic polymers according to the invention are preferably used in water-based preparations containing surface-active compounds. Preferred surface-active compounds are anionic, zwitterionic, amphoteric and/or non-ionic surfactants.

10 Suitable anionic surfactants for the hair-treatment preparations according to the invention are any anionic surface-active compounds suitable for use on the human body. They are characterized by a water-solubilizing anionic group such as, for example, a carboxylate, sulfate, sulfonate, or phosphate group and a lipophilic alkyl group containing about 10 to 22 carbon atoms. In addition, glycol ether or polyglycol ether groups, ester, ether, and 15 amide groups and also hydroxyl groups may be present in the molecule. Examples of suitable anionic surfactants are the sodium, potassium, and ammonium salts and the mono-, di- and tri-alkanolammonium salts - containing 2 or 3 carbon atoms in the alkanol group - of:

20 - linear fatty acids containing 10 to 22 carbon atoms (soaps);
- ether carboxylic acids corresponding to the formula R-O-(CH₂CH₂O)_x-CH₂-COOH, in which R is a linear C₁₀₋₂₂ alkyl group and x = 0 or 1 to 10;
25 - acyl sarcosides containing 10 to 18 carbon atoms in the acyl group;
- acyl taurides containing 10 to 18 carbon atoms in the acyl group;
- acyl isethionates containing 10 to 18 carbon atoms in the acyl group;
30 - sulfosuccinic acid mono- and di-alkyl esters containing 8 to 18 carbon atoms in the alkyl group and sulfo- succinic acid monoalkyl polyethoxyl esters containing 8 to 18 carbon atoms in the alkyl group and 1 to 6 ethoxyl groups;
35 - linear alkanesulfonates containing 12 to 18 carbon atoms;

- linear α -olefin sulfonates containing 12 to 18 carbon atoms;
- α -sulfofatty acid methyl esters of fatty acids containing 12 to 18 carbon atoms;
- 5 - alkylsulfates and alkyl polyglycol ether sulfates corresponding to the formula $R-O(CH_2-CH_2O)_x-OSO_3H$, in which R is a preferably linear alkyl group containing 10 to 18 carbon atoms and $x = 0$ or 1 to 12;
- mixtures of surface-active hydroxysulfonates according
- 10 to DE-OS 37 25 030;
- sulfated hydroxyalkyl polyethylene and/or hydroxyalkylene propylene glycol ethers according to DE-OS 37 23 254;
- esters of tartaric acid and citric acid with alcohols
- 15 which are adducts of about 2 to 15 molecules of ethylene oxide and/or propylene oxide with fatty alcohols containing 8 to 22 carbon atoms.

Preferred anionic surfactants are alkyl sulfates and alkyl polyglycol ether sulfates containing 10 to 18 carbon atoms in the alkyl group and up to 12 glycol ether groups in the molecule.

Zwitterionic surfactants are surface-active compounds which contain at least one quaternary ammonium group and at least one $-COO^-$ or $-SO_3^-$ group in the molecule. Particularly suitable zwitterionic surfactants are the so-called betaines, such as N-alkyl-N,N-dimethyl ammonium glycinate, for example coconut oil alkyl N,N-dimethyl ammonium glycinate, N-acylaminopropyl-N,N-dimethyl ammonium glycinate, for example coconut oil acylaminopropyl-N,N-dimethyl ammonium glycinate, and 2-alkyl-3-carboxymethyl-3-hydroxyethyl imidazolines containing 8 to 18 carbon atoms in the alkyl or acyl group, and also coconut oil acylaminoethyl hydroxyethyl carboxymethyl glycinate.

Amphoteric surfactants are understood to be surface-active compounds which, in addition to a C_{8-18} alkyl or acyl group, contain at least one free amino group and at least one $-COOH-$ or $-SO_3H-$ group in the molecule and which are

capable of forming inner salts. Examples of suitable amphoteric surfactants are N-alkyl glycines, N-alkylamino-propionic acids, N-alkylaminobutyric acids, N-alkyliminodipropionic acids, N-hydroxyethyl-N-alkylamidopropyl glycines, N-alkyl taurines, N-alkyl sarcosines, 2-alkylamino-propionic acids, and alkylaminoacetic acids containing about 8 to 18 carbon atoms in the alkyl group.

5 Nonionic surfactants are, above all, the adducts of 2 to 20 moles of ethylene oxide with preferably linear alcohols containing 12 to 18 carbon atoms, with alkylphenols containing 8 to 15 carbon atoms in the alkyl group, with fatty acids containing 12 to 18 carbon atoms, with fatty acid partial glycerides, with fatty acid sorbitan partial esters, with fatty alkanolamides, and with methyl glucoside 10 fatty acid esters. Other suitable nonionic surfactants are alkyl(oligo)glycosides, alkylamine oxide surfactants, and fatty acid alkanolamides.

15 Cationic surfactants may also be present in the preparations according to the invention providing they are compatible with the other components, for example anionic surfactants. Such cationic surfactants are known, for example, from DE-OS 34 42 175.

20 The preparations according to the invention preferably contain surface-active compounds in quantities of 0.1 to 25 40 % by weight, based on the preparation as a whole.

25 By virtue of their favorable hair-conditioning and hair-setting properties and their compatibility with the substances typically used in hair-treatment preparations, the zwitterionic polymers according to the invention are suitable as setting and hair-conditioning components in any 30 standard water-based hair-washing and hair-care preparations, such as for example shampoos, after-rinses, hair setting lotions, hair setting gels, and water-based coloring, permanent-wave, and permanent-wave fixing preparations.

35 Accordingly, the water-based hair-washing and hair-care preparations according to the invention may contain

any standard auxiliaries and additives for the particular application envisaged in addition to the compulsory zwit-terionic polymers.

For hair rinses, such auxiliaries and additives are, for example, cationic surfactants, more particularly surface-active quaternary ammonium salts, fatty alcohols containing 12 to 22 carbon atoms, fatty acid partial glycerides, cosmetic oil and fatty components, and water-soluble polymers having a thickening effect. For hair setting lotions and hair setting gels, the auxiliaries and additives in question are, for example, cationic surfactants, cationic, nonionic, or anionic polymers, and lower alcohols. Hair-dyeing preparations contain substantive dyes or oxidation dye precursors, anionic or nonionic surfactants, ammonia or alkanolamines, and, optionally, antioxidants. Permanent-wave fixing preparations contain an oxidizing agent, for example H_2O_2 , H_2O_3 adducts, or potassium bromate, and also anionic or nonionic surfactants.

The preparations according to the invention preferably have a pH value of 4 to 10 and, more preferably, 5 to 9.

The following Examples are intended to illustrate the invention without limiting it in any way.

Examples

1. Preparation of a polymer of acrylamidopropyl trimethyl ammonium chloride and acrylic acid in a molar ratio of 3:1 (polymer P1).

201.17 kg of water, 89.59 kg of a 60% by weight aqueous solution of acrylamidopropyl trimethyl ammonium chloride and 6.25 kg of acrylic acid were introduced into a reactor equipped with an impeller stirrer, a heating and cooling system, a reflux condenser, and a temperature measuring instrument. A pH value of 3.4 was spontaneously established. The solution was purged with nitrogen and then heated to 60° C. Solutions of 0.06 kg of azo-bis-(amidinopropane)-dihydrochloride in 1.00 kg of water, 0.024 kg of potassium peroxodisulfate in 1,000 kg of water, and 0.012 kg of sodium disulfite in 1,000 kg of water were then suc-

cessively added to the mixture with stirring. Only slight heating occurred. The reaction mixture was heated to 80 - 85 ° C and kept at that temperature for 4 hours. The polymerization was then terminated. The viscous solution was 5 cooled to 30-40 ° C and neutralized with 5,000 kg of 45% aqueous sodium hydroxide.

10 The clear colorless polymer solution had the following characteristic data: pH value 6.9, dry matter 20%, product viscosity 13,800 mPa s, intrinsic viscosity 220 ml/g (in 10% NaCl solution).

2. Applications Examples

2.1. Hair rinse No. 1

Components	% by weight
Fatty alcohol (C ₁₂₋₁₄) poly(3EO)glycol ether sulfate, Na salt, 28% aqueous solution	5.0
Coconut oil acyl(C ₁₂₋₁₈)aminopropyl dimethyl glycine, 30% aqueous solution	1.0
Polymer P1 (20% active substance in water)	2.5
Water	ad 100

20 The rinse is in the form of a cloudy solution. The wet combability of hair treated with this rinse was very good. No adverse effect on the hair or static charging of the hair was observed.

2.2 Hair rinse No. 2

Components	% by weight
Fatty alcohol (C ₁₂₋₁₄) poly(3 EO) glycol ether sulfate, Na salt, 28% aqueous solution	5.0
Dehyton® AB 30 ¹	1.0
Polymer P1 (20% active substance in water)	2.5
Water	ad 100

1 Fatty amine derivative of betaine structure, approx. 30% active substance in water, CTFA name: coco-betaine (HENKEL)

35 The rinse is in the form of a cloudy solution. The wet combability of hair treated with this rinse was very

good.

2.3 Hair rinse No. 3

	Components	† by weight
5	Sulfosuccinic acid semiester based on a C ₁₂₋₁₄ alkyl poly(3 EO)glycol ether, di-sodium salt (40% active substance in water, CTFA name: disodium laurethsulfosuccinate	0.9
	Texapon® K14 S spez. ²	1.2
	Dehyton® AB 30	1.0
10	Polymer P1 (20% active substance in water)	2.5
	Water	ad 100

² Sodium lauryl myristyl ether sulfate, about 30% active substance in water (HENKEL)

The wet combability of hair treated with this rinse was good to very good.

2.4 Hair rinse No. 4

	Components	† by weight
20	Sulfosuccinic acid semiester based on a C ₁₂₋₁₄ alkyl poly(3 EO)glycol ether, di-sodium salt (40% active substance in water), CTFA name: disodium laurethsulfosuccinate	1.0
	Dehyton® AB 30	7.5
	Polymer P1 (20% active substance in water)	2.5
	Water	ad 100

25 The rinse is present in the form of an almost clear solution. The wet combability of hair treated with this rinse was very good.

2.5 Hair rinse No. 5

	Components	† by weight
30	C ₁₆₋₁₈ fatty alcohol	3.0
	Coconut oil acyl(C ₁₂₋₁₈)aminopropyl dimethyl glycine, 30% aqueous solution	8.0
	Fatty alcohol (C ₁₂₋₁₆) poly(3 EO)glycol ether sulfate, Na salt, 28% aqueous solution	5.0
35	Polymer P1 (20% active substance in water)	2.5
	Water	ad 100

To prepare this hair rinse, the mixture of surfactants and polymer was introduced into the molten fat phase and emulsified therein. The wet combability of hair treated with this rinse was excellent.

5	2.6 Hair shampoo No. 1	# by weight
Components		
	Fatty alcohol (C_{12-14}) poly(3 EO)glycol ether sulfate, Na salt, 28% aqueous solution	50.0
10	Coconut oil acyl(C_{12-18})aminopropyl dimethyl glycine, 30% aqueous solution	10.0
	Polymer P1 (20% active substance in water)	5.0
	Water	ad 100

The wet combability of hair shampooed with this preparation was excellent.

15	2.7 Hair shampoo No. 2	# by weight
Components		
	Fatty alcohol (C_{12-14}) poly(3 EO)glycol ether sulfate, Na salt, 28% aqueous solution	45.0
20	Coconut oil acyl(C_{12-18})aminopropyl dimethyl glycine, 30% aqueous solution	15.0
	Akypo® RLM 100 NV ³	5.0
	Polymer P1 (20% active substance in water)	5.0
	Water	ad 100

25	3 Aqueous solution of C_{12-14} alkyl-O- $(CH_2-CH_2-O)_{10}-CH_2-$ COOONa, 22% active substance (CHEM-Y)
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This shampoo not only freed the hair from soil and grease, it also had a distinct conditioning effect on wet hair and left dry hair with body and volume.

To quantify the effect obtained by the polymer, a 15 cm long strand of hair (2 g) was wound onto a glass tube having a external diameter of 1.7 cm, fixed and treated with 0.2 g of the shampoo. The hair strand was then rinsed with water and dried. A measure of the stability of the curl obtained after withdrawal of the glass rod is the curl retention value. The curl retention value is defined as $[(l-l_r)/(l-l_o)] * 100\%$ where l is the length of the hair

strand (15 cm), l_0 is the length of the hair curl immediately after drying and l_x is the length of the hair curl after storage for 48 h under constant conditions (30°C/40% relative air humidity) in a drying cabinet. The curls treated with the shampoo according to the invention had a curl retention value of 94.7% whereas curls treated with a similar shampoo to which polymer P1 had not been added showed a curl retention of only 87.1%.

2.8 Hair shampoo No. 3

		% by weight
10	Components	
	Texapon® K14 S spez.	15.0
	Sulfosuccinic acid semiester based on a C ₁₂₋₁₄ alkyl polyglycol (3 EO) ether, disodium salt (40% active substance in water), CTFA name: disodium laurethsulfosuccinate	12.0
15	Ethoxylated (9 EO) palm kernel oil fatty acid	1.0
	Alkyl glucoside APG-600	4.0
	Dehyton® CB ⁵	9.7
20	Polymer P1 (20% active substance in water)	5.0
	Water	ad 100
	4 Aqueous solution of RO(Z) _x with Z = glucose, x = 1.4 and R = n-alkyl(C ₁₂₋₁₄), (50% active substance) (HORIZON)	
25	5 Aqueous solution of a fatty amine derivative of betaine structure, CTFA name: coco-betaine (approx. 31% active substance, approx. 6.5% NaCl) (HENKEL)	

The shampoo is clear and colorless. This shampoo had an excellent conditioning effect on the hair.

30 2.9 Hair shampoo No. 4

		% by weight
	Components	
	Sulfosuccinic acid semiester based on a C ₁₂₋₁₄ alkyl polyglycol (3 EO) ether, disodium salt (40% active substance in water), CTFA name: disodium laurethsulfosuccinate	12.0
35	Ethoxylated (9 EO) palm kernel oil fatty acid	1.0
	Dehyton® CB	10.0

Eucarole® TA ⁶	20.0
Polymer P1 (20% active substance in water)	1.2
Water	ad 100
6 Aqueous solution of sodium laureth-7-tartrate, 25%	
5 active substance (ROL)	

5 This clear shampoo was distinguished in particular by an excellent conditioning effect coupled with a good cleaning effect.

2.10 Hair shampoo No. 5

10	Components	± by weight
10	Sulfosuccinic acid semiester based on a C ₁₂₋₁₄ alkyl polyglycol (3 EO) ether, disodium salt (40% active substance in water), CTFA name: disodium laurethsulfosuccinate	15.0
15	Dehyton® CB	12.0
	Alkyl glucoside APG-600	4.0
	Polymer P1 (20% active substance in water)	1.2
20	Water	ad 100

20 This clear shampoo left the shampooed hair with very good wet combability.

CLAIMS

1. Water-based hair-treatment preparations containing zwitterionic polymers, characterized in that the zwitterionic polymers are essentially made up of

5 A) monomers containing quaternary ammonium groups corresponding to general formula (I)

$$R^1-CH=CR^2-CO-Z-(C_nH_{2n})-N^{(+)R^3R^4R^5} A^{(-)} \quad (I)$$
in which R^1 and R^2 independently of one another represent hydrogen or a methyl group and R^3 , R^4 , and R^5 independently of one another represent C_{1-4} alkyl groups, Z is an NH group or an oxygen atom, n is an integer of 2 to 5, and $A^{(-)}$ is the anion of an organic or inorganic acid
and

10 B) monomeric carboxylic acids corresponding to general formula (II)

$$R^6-CH=CR^7-COOH \quad (II)$$
in which R^6 and R^7 independently of one another are hydrogen or methyl groups.

20 2. Preparations as claimed in claim 1, characterized in that the zwitterionic polymers consist of monomers of type (A) and monomers of type (B) in a molar ratio of 60:40 to 95:5 and, more particularly, 75:25 to 95:5.

25 3. Preparations as claimed in claim 1 or 2, characterized in that, in the monomers of type (A), R^3 , R^4 and R^5 are methyl groups, Z is an NH group, and $A^{(-)}$ is a halide, methoxysulfate, or ethoxysulfate ion.

30 4. Preparations as claimed in any of claims 1 to 3, characterized in that the monomer of type (A) is acrylamido-propyl trimethyl ammonium chloride.

35 5. Preparations as claimed in any of claims 1 to 4, characterized in that the monomer of type (B) is acrylic acid.

6. Preparations as claimed in any of claims 1 to 5, characterized in that they contain the zwitterionic polymers in quantities of 0.1 to 10% by weight and more particularly in

quantities of 1 to 5% by weight, based on the preparation as a whole.

5. Preparations as claimed in any of claims 1 to 6, characterized in that they contain at least one surface-active compound selected from the group of anionic, zwitterionic, amphoteric and nonionic surfactants.

8. Preparations as claimed in claim 7, characterized in that they contain the surface-active compounds in quantities of 0.1 to 40% by weight, based on the preparation as 10 a whole.

9. Preparations as claimed in any of claims 1 to 8, characterized in that they have a pH value of 4 to 10 and, more particularly, 5 to 9.

10. Preparations as claimed in any of claims 1 to 9, characterized in that they are formulated as shampoos or 15 rinses.

11. The use of the preparations claimed in any of claims 1 to 10 for the treatment of hair.